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(54) Method for preparation of α -amino-naphtho[2,1-d]thiazol-mono-/di-/OH-sulfonic acids

(57) A simple method is described for preparation of α -amino-naphtho[2,1-d]thiazol-mono-/di-/OH-sulfonic acids, in which easily accessible 2-amino-naphthalin-mono-/di-/tri-sulfonic acids or 2-amino-OH-sulfonic acids are reacted with thiocyanate salts in the presence of an oxidizing agent in aqueous-alcoholic medium in a "one pot" method.

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Area of application of the invention

The invention concerns a method for preparation of heterocyclic five-ring compounds of the naphthalin series containing sulfonic acid groups. They can be used, for example, as intermediates in the preparation of paints.

Characterization of the known technical solutions

α -amino-naphtho[2,1-d]thiazol-sulfonic acids have been mentioned thus far as diazotation components in two derivatives in DD 113 760; but nothing was reported there about their preparation.

Purpose of the invention

The purpose of the invention is to create a technologically simple method based on easily accessible starting substances for the preparation of α -amino-naphtho[2,1-d]thiazol-mono-/di-/OH-sulfonic acids, which furnishes products in good quality and good yield in a type of "one pot" method, and wherein such precursor products are used where, for technological reasons, no portions of carcinogenic substances such as β -naphthylamine can be present.

Presentation of the essence of the invention

The basic problem of the invention is to create a technologically simple method for the preparation of 2-amino-naphtho[2,1-d]thiazol-mono-/di-/OH-sulfonic acids.

According to the invention, the problem is solved by using 2-aminonaphthalin-sulfonic acids such that either one or more sulfonic acid groups and possibly an OH group are

present in the core of the naphthalin ring, which carries no amino group, or wherein one uses β -aminonaphthalin-sulfonic acids which carry a sulfonic acid group in the α -position and furthermore must also have an additional sulfonic acid group in the 5-position.

Thus, one uses only such technical starting compounds as are considered toxicologically safe by virtue of their multiple content of hydrophilic groups, such as OH and SO_3H groups, and especially by virtue of their technical preparation. According to the invention, the problem is solved in that β -amino-naphthalin-sulfonic acids, which may also contain OH groups, are reacted in aqueous alcoholic medium with thiocyanate salts in the presence of an oxidizing agent and aqueous acid.

A further benefit according to the invention is that, when one uses such β -amino-naphthalin di- or tri- sulfonic acids where there is a sulfonic acid in α -position to the β -positioned amino group, this sulfonic acid in the α -position is eliminated during the ring closure reaction.

During the reaction, a transient heating of the reaction mixture occurs; no lengthy boiling process is necessary. It is enough to heat the reaction mixture to 60-65°C for 15-20 minutes. The method can be carried out very easily and furthermore is very time-saving. The desired heterocyclic acids are sometimes obtained in very good yields.

Application samples

Example 1

2-amino-naphtho[2,1-d]thiazol-6-sulfonic acid

- a) To a solution of 30 g of potassium thiocyanate in 300 ml of methanol there is added 25 g of concentrated hydrochloric acid and 31.7 g (0.1 mole) of 2-amino-naphthalin-1,5-disulfonic acid. To this suspension, at room temperature, is slowly dripped in a solution of 30 ml of perhydrol in 40 ml of methanol, and this is then heated to 60-65°C for 30 minutes. After cool down, the reaction mixture is reacted with concentrated aqueous solution of ammonia until a weak alkaline reaction occurs, and it is filtered. From the filtrate, the sulfonic acid is precipitated with concentrated HCl, aspirated, and dried. The yield is 90% of theoretical.

- b) Starting with 22.3 g (0.1 mole) of 2-amino-naphthalin-5-sulfonic acid, this sulfonic acid is obtained in a yield of 90%, as described in example 1a).

Example 2

2-amino-naphtho[2,1-d]thiazol-7-sulfonic acid

- a) Starting with 22.3 g (0.1 mole) of 2-amino-naphthalin-6-sulfonic acid, the desired heterocyclic sulfonic acid is obtained in a yield of 85% in a manner similar to that described in example 1.
- b) From 31.7 g (0.1 mole) of 2-amino-naphthalin-1,6-disulfonic acid, the thiazol-sulfonic acid is obtained in a yield of 85% as described in example 1.

Example 3

2-amino-naphtho[2,1-d]thiazol-9-sulfonic acid

One reacts 22.3 g (0.1 mole) of 2-amino-naphthalin-8-sulfonic acid, as described in example 1, and obtains the acid in a yield of 54%.

Example 4

- a) The heterocyclic acid is obtained when starting with 31.7 g (0.1 mole) 2-amino-naphthalin-1,7-disulfonic acid and reacting this as described in example 1. It is obtained in a yield of 77%.
- b) If one reacts 22.3 g (0.1 mole) of 2-amino-naphthalin-7-sulfonic acid, as described in example 1, the desired sulfonic acid is obtained in a yield of 78%.

Example 5

2-amino-naphtho[2,1-d]thiazol-6,8-disulfonic acid

- a) If one starts with 31.7 g (0.1 mole) of 2-amino-naphthalin-5,7-disulfonic acid, then the desired acid is obtained in a yield of 62%, as described in example 1.
- b) Starting with 38.3 g (0.1 mole) of 2-amino-naphthalin-trisulfonic acid (-1,5,7), the thiazol-sulfonic acid is obtained in a yield of 68%, as described in example 1.

Example 6

2-amino-naphtho[2,1-d]thiazol-7,9-disulfonic acid

If 31.7 g (0.1 mole) of 2-amino-naphthalin-6,8-disulfonic acid (amino-G-acid) is reacted as described in example 1, the thiazol-disulfonic acid accrues in a yield of 43%.

Example 7

2-amino-naphtho[2,1-d]thiazol-6-hydroxy-8-sulfonic acid

Starting with 23.9 g (0.1 mole) of 2-amino-naphthalin-5-OH-7-sulfonic acid (I-acid), the corresponding hydroxy-sulfonic acid is obtained in a yield of 84%, as described in example 1.

Example 8

2-amino-naphtho[2,1-d]thiazol-4,7-disulfonic acid

If 31.7 g (0.1 mole) of 2-amino-naphthalin-3,6-disulfonic acid (amino-R-acid) is reacted as described in example 1, the corresponding disulfonic acid is obtained in a yield of 54%.

Example 9

2-amino-naphtho[2, -d]thiazol-5,9-disulfonic acid

One reacts 31.7 g (0.1 mole) of 2-amino-naphthalin-4,8-disulfonic acid as described in example 1. The thiazol-disulfonic acid is obtained in a yield of 51%.

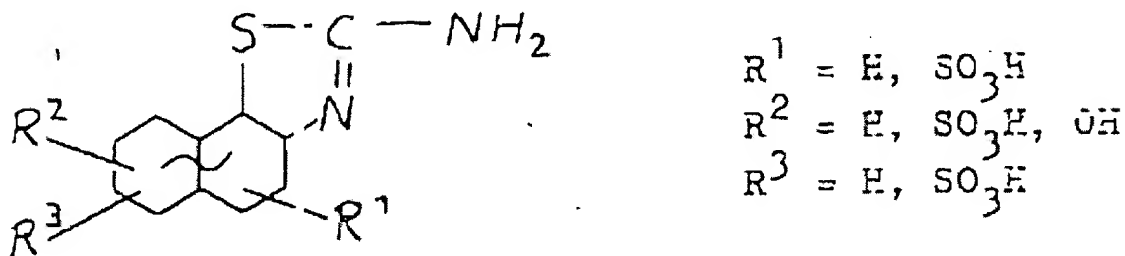
Example 10

2-amino-naphtho[2,1-d]thiazol-9-OH-7-sulfonic acid

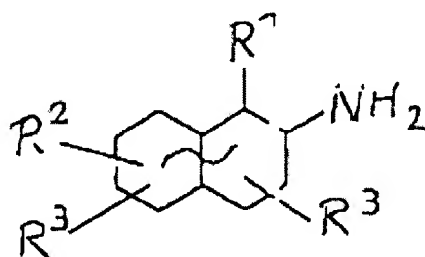
Starting with 23.9 g (0.1 mole) of 2-amino-naphthalin-8-OH-6-sulfonic acid (T-acid), one obtains the hydroxy-naphthothiazol-sulfonic acid in a yield of 60%.

Claims of the invention

1. Method for preparation of α -amino-naphtho[2, -d]thiazol-mono/di-/OH-sulfonic acids of formula I



characterized in that one reacts β -amino-naphthalin-mono/di-/tri-sulfonic acids or β -amino-naphthalin-hydroxy-sulfonic acids of formula II



$$\begin{aligned} R^1 &= \text{H}, \text{SO}_3\text{H} \\ R^2 &= \text{H}, \text{SO}_3\text{H}, \text{OH} \\ R^3 &= \text{H}, \text{SO}_3\text{H} \end{aligned}$$

where

R^1, R^2 or R^3 must always
be a SO_3H group

with thiocyanate salts in presence of substances promoting the thiocyanation in the presence of an oxidizing agent to form β -amino-naphtho[2,1-d]thiazol-mono-/disulfonic acids or hydroxy-sulfonic acids of formula I.

2. Method per Claim 1, characterized in that these reactions are carried out in aqueous-alcoholic medium.